

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/010771

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/48 A61K7/075 A61K47/10 A61K31/573

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 078 638 A (DRAGOCO GERBERDING & CO AKTIENGESELLSCHAFT) 28 February 2001 (2001-02-28) claims 1,9,10 paragraph '0033!	1-38
X	WO 03/011244 A (L'OREAL; SIMONNET, JEAN-THIERRY) 13 February 2003 (2003-02-13) claims 1,11 page 1, line 21 page 8, lines 11-16	1,5-15, 35,37
	----- -/-- -----	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

3 May 2005

Date of mailing of the international search report

17/05/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Hauss, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/010771

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 28 February 2002 (2002-02-28), FUKUDA, YASUHIRO ET AL: "Skin preparations containing 1,2-pentanediol as percutaneous absorption enhancer" XP002326555 retrieved from STN Database accession no. 2002:235862 abstract -& JP 2002 087926 A (POLA CHEMICAL INDUSTRIES, INC., JAPAN) 27 March 2002 (2002-03-27) claims 1,7 paragraph '0016!; example 4</p>	<p>1,5-15, 35,37</p>
X	<p>EP 0 321 951 A (L'OREAL) 28 June 1989 (1989-06-28) claims example 5</p>	<p>1-15,35, 37</p>
E	<p>WO 2005/004830 A (THE PROCTER & GAMBLE COMPANY; NONAKA, GEN; TANAKA, HIDEKAZU) 20 January 2005 (2005-01-20) example 3</p>	<p>1,5-7, 10,13, 35,37</p>

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2004/010771

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: —
because they relate to subject matter not required to be searched by this Authority, namely:
Although claims 37 and 38 are directed to a method of treatment of the human/animal body, the search has been carried out and based on the alleged effects of the compound/composition.
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/010771

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1078638	A	28-02-2001	US 6274124 B1	14-08-2001
			AU 5194700 A	22-02-2001
			BR 0003897 A	03-04-2001
			CA 2316329 A1	20-02-2001
			EP 1078638 A1	28-02-2001
			ID 26948 A	22-02-2001
			JP 2001072531 A	21-03-2001
			PL 341803 A1	26-02-2001
WO 03011244	A	13-02-2003	FR 2827764 A1	31-01-2003
			EP 1414403 A1	06-05-2004
			WO 03011244 A1	13-02-2003
			US 2004186085 A1	23-09-2004
JP 2002087926	A	27-03-2002	NONE	
EP 0321951	A	28-06-1989	LU 87091 A1	07-07-1989
			AT 99918 T	15-01-1994
			CA 1303997 C	23-06-1992
			DE 3887117 D1	24-02-1994
			DE 3887117 T2	28-04-1994
			EP 0321950 A1	28-06-1989
			EP 0321951 A1	28-06-1989
			JP 1203315 A	16-08-1989
			JP 2712105 B2	10-02-1998
			JP 1203327 A	16-08-1989
			US 5643898 A	01-07-1997
WO 2005004830	A	20-01-2005	WO 2005004830 A1	20-01-2005
			AU 2003243573 A1	28-01-2005
			US 2005019283 A1	27-01-2005

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 078 638 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.02.2001 Bulletin 2001/09

(51) Int. Cl.⁷: **A61K 47/10**, **A61K 7/42**,
A61K 7/48

(21) Application number: **00116508.3**

(22) Date of filing: **31.07.2000**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **20.08.1999 US 378402**

(71) Applicant:
Dragoco Gerberding & Co Aktiengesellschaft
37603 Holzminden (DE)

(72) Inventor: **Vollhardt, Jürgen**
Lincoln Park, New Jersey (US)

(74) Representative:
Eisenführ, Spelser & Partner
Martinistrasse 24
28195 Bremen (DE)

(54) **Additive for improving the water resistance of cosmetic or dermatological formulations**

(57) A method for imparting water resistance to or improving water resistance of a cosmetic or dermatological formulation, comprising adding an water resistance enhancing effective amount of 1,2-pentanediol to the otherwise conventional cosmetic or dermatological formulation comprising at least one cosmetic and/or dermatological active agent in a cosmetically and/or pharmaceutically acceptable carrier for topical application to the skin of humans.

EP 1 078 638 A1

Description

Background of the Invention

5 Field of the Invention

[0001] The present invention relates to cosmetic or dermatological formulations, in particular UV radiation protection formulations.

10 [0002] The skin is an important, but at the same time sensitive, human organ, the care of which is essential for physical and psychological well-being. A large number of skin care compositions have been developed, which are supplied as creams, lotions, oils or gels and contain special skin care active ingredients.

[0003] Cosmetic and dermatological skin care compositions are primarily used in order to intensify or restore the natural function of skin as a barrier against environmental influences (for example dirt, chemicals, microorganisms) and against the loss of endogenous substances (for example water, natural fats, electrolytes).

15 [0004] If this function is impaired, increased absorption of toxic or allergenic substances or attack by microorganisms and, as a consequence, toxic or allergic skin reactions may occur.

[0005] The aim of cosmetic skin care is furthermore to compensate the loss of fats and water from the skin caused by daily washing. This is important especially if the natural regeneration capacity is inadequate. Skin care products furthermore should protect against environmental influences, in particular sun and wind, and delay the signs of ageing of the skin.

[0006] The damaging effect of the ultraviolet part of solar radiation on the skin is generally known. While rays having a wavelength in the range from 200-280 nm (the so-called UVC range) are completely absorbed by the ozone layer in the earth's atmosphere, rays in the range between 280 nm and 315 nm, the so-called UVB range, cause erythema, simple sunburn or even burns of greater or lesser severity on the skin.

25 [0007] Numerous water-soluble or lipid-soluble organic UV filter substances (chemical sunscreen filter substances) are known for protection against UVB radiation, most of these substances being derivatives of 3-benzylidenecamphor, of 4-aminobenzoic acid, of cinnamic acid, of salicylic acid, of benzophenone and also of 2-phenylbenzimidazole (e.g. 2-phenylbenzimidazole-5-sulfonic acid sodium salt). Other examples of UV filter substances can be found in the literature.

30 [0008] UV filter substances are also important for the wavelength range between about 315 and 400 nm, the so-called UVA range, since such rays can also cause damage. It has thus been proved that UVA radiation leads to damage to the elastic and collagenic fibers of the connective tissue, which makes the skin age prematurely and is to be regarded as a cause of numerous phototoxic and photoallergic reactions. The damaging influence of UVB radiation may be intensified by UVA radiation.

35 [0009] UV radiation can also lead to photochemical reactions, the photochemical reaction products then intervening in skin and cell metabolism.

[0010] Such photochemical reaction products are chiefly free radical compounds, for example hydroxyl radicals, hydroperoxy radicals and superoxide ions. Further damage is caused by free radical photo-products which are formed in the skin itself and bear high reactivity. However, even singlet oxygen, an excited state of the oxygen molecule which is not in free radical form, can occur with UV irradiation, as can short-lived epoxides and many others. Singlet oxygen, for example, is distinguished from the triplet oxygen usually present (free radical base state) by an increased reactivity. Nevertheless, excited, reactive (free radical) triplet states of the oxygen molecule also exist.

[0011] To prevent these reactions, antioxidants and/or agents which trap the radicals can be incorporated into the cosmetic or dermatological formulations, typically in addition to organic UV filter substances.

45 [0012] Furthermore, coated or uncoated inorganic pigments which are known to be used in sunscreen products can help to protect the skin from UV rays. Most inorganic pigments used in cosmetics to protect the skin from UV rays are UV absorbers or UV reflectors. These are oxides of titanium, zinc, iron, zirconium, silicon, manganese, aluminium, cerium and mixtures thereof, as well as modifications. Inorganic pigments are typically used in addition to organic UV filter substances.

50 [0013] Numerous sunscreen compositions (sun protection products) are known for protection against the detrimental effects of exposure to sunlight (UVA and UVB). For various reasons associated especially with being more pleasant to use (gentleness, emollience, ease of application and the like) the sunscreen compositions currently available are typically (but not always) oil-in-water emulsions (namely, a cosmetically acceptable vehicle, carrier or diluent) comprising an aqueous continuous dispersion phase and an oily discontinuous dispersed phase which contain, at various concentrations, one or more organic UV filter substances which are capable of selectively absorbing harmful UV radiation, these filter substances being selected as a function of the degree of desired protection. However, one of the problems presented by this type of sunscreen composition is, in particular, the fact that, once they have been applied to the skin in the form of a film by the users thereof, they have relatively little resistance to water.

[0014] Light protection formulations are required and used particularly frequently on bathing beaches and in open-air swimming pools. It is in this case desirable for the light protection formulation to be largely water-resistant, that is to say for it to be washed off from the skin to only a small extent, if at all.

[0015] Higher light protection factors, that is to say, for example, those situated above SPF 15, can in general be achieved only by larger amounts of UV filter substances. If a sunscreen product is also still to have a high light protection factor after bathing, the UV filter substance in particular must be retained on the skin.

[0016] It is in itself already troublesome if the sunscreen product has to be applied again after bathing. During bathing itself, under certain circumstances the use of a light protection formulation which can be washed off is even irresponsible and harmful to the skin, since water absorbs light in the UVA and UVB range poorly, and consequently represents no noticeable UV protection, not even for submerged areas of skin.

[0017] Accordingly, a major object of the present invention is the provision of novel cosmetic or dermatological compositions, in particular sunscreen compositions, which have increased water resistance.

[0018] By the term "water resistance" is intended the stability, activity or effect over time of the active ingredient(s) of a given cosmetic or dermatological formulation.

[0019] With respect to sunscreen formulations the term "water resistance" is intended the stability over time of the degree of protection in the UVA and/or UVB ranges of sunscreen composition subjected (after application to the skin) to contact with water. The solar protection associated with a given composition is characterized by assigning it a sun protection factor (or SPF) which is mathematically expressed by the ratio of the exposure time necessary to attain the erythematous threshold (minimal erythema dose) with the UV screen to the time necessary to attain the erythematous threshold without UV screen.

[0020] With respect to formulations comprising other (non-UV-protective) cosmetic and/or dermatological agent(s) the term "water resistance" refers to the activity or effect over time of the respective agent(s) of a formulation subjected (after application to the skin) to contact with water.

[0021] A further object of the invention is the provision of a method for imparting water resistance to or improving water resistance of a cosmetic or dermatological formulation comprising a cosmetic or dermatological agent in a cosmetically and/or pharmaceutically acceptable carrier (this term comprising all kinds of carriers, vehicles, diluents and the like) for application, in particular topical application, to the skin of humans or animals.

Summary of the Invention

[0022] Surprisingly, it has now been found that by adding an amount of 1,2-pentanediol the water resistance of a (conventional) cosmetic or dermatological formulation comprising at least one cosmetic and/or dermatological active agent in a cosmetically and/or pharmaceutically acceptable carrier for topical application to the skin of humans or animals can be imparted or improved.

[0023] The 1,2-pentanediol preferably represents more than 0.5 % by weight, relative to the total weight of the resulting water resistant composition, more preferably more than 3% and most preferably from 3 to 6%.

[0024] From the European Patent Specification 0 665 904 B1 (Dragoco) it is known that 1,2-pentanediol is suitable as skin-moisture-regulating active ingredient in cosmetic product. However, 1,2-pentanediol is characterized by a virtually unlimited miscibility with water. Thus, it was absolutely unexpected that 1,2-pentanediol can improve the water resistance of a cosmetic or dermatological formulation. It had rather been expected that it would be washed off the skin easily and could therefore have no effect on the water resistance properties of a given formulation. Further-more, 1,2-propanediol and 1,2-hexanediol do not show a water resistance enhancing effect. As shown below in detail, addition of 1,2 hexandiol rather decreases the water resistance of a cosmetic formulation.

[0025] The carrier of the formulations according to the present invention can be in the form of a homogeneous phase formulation or in the form of an emulsion including, but not limited to, oil-in-water, water-in-oil and multiple phase emulsions. These emulsions can cover a broad range of consistencies including thin lotions (which can also be suitable for spray or aerosol delivery), creamy lotions, light creams, heavy creams, and the like. Other suitable topical carriers include anhydrous liquid solvents such as oils and alcohols; aqueous-based single phase liquid solvents (e.g. hydro-alcoholic solvent systems); anhydrous solids and semisolids (such as gels and sticks); and aqueous based gel and mousse systems. Examples of carrier systems useful in the present invention are described in the following four references all of which are incorporated herein by reference in their entirety: "Sun Products Formulary" Cosmetics & Toiletries, vol. 105, pp. 122-139 (December 1990); "Sun Products Formulary", Cosmetics & Toiletries, vol. 102, pp. 117-136 (March 1987); U.S.Pat. No. 4,960,764 to Figueroa et al., issued Oct. 2, 1990; and U.S. Pat. No. 4,254,105 to Fukuda et al., issued Mar. 3, 1981.

[0026] With reference to sunscreen formulations, the carriers, in total, typically comprise from about 0.1% to about 99.87. by weight of the sunscreen compositions of the present invention (prepared according to the present invention), preferably from about 80% to about 99%, and most preferably from about 85% to about 95%.

[0027] A preferred topical carrier of the compositions of the instant invention is an oil-in-water type emulsion. The

pH of these oil-in-water emulsion compositions herein is preferably in the range of from about 4.5 to about 9. Additionally, the mean particle size of the dispersed oil phase materials (e.g. sunscreen agent, polymer, perfumes, etc.) dispersed in the aqueous phase of these oil-in-water emulsion compositions may be in the range of from about 5 to about 10 microns with greater than about 75% of the particles being less than about 12 microns.

[0028] The invention is of particular relevance with respect to sunscreen products, i.e. cosmetic or dermatological formulations which comprise, as a cosmetic or dermatological agent, an organic UV filter substance.

[0029] Correspondingly, there is provided a novel method for providing enhanced protection to the skin of humans or animals from the effects of ultraviolet radiation, namely a method comprising topically applying to the skin of the human or animal an effective amount of a sunscreen composition comprising a water resistance improving effective amount of 1,2-pentanediol

[0030] The organic UV filter substances that can be employed within the concept of the present invention are those typical in the art, in particular those mentioned above.

[0031] A formulation suitable for addition of 1,2-pentanediol may, in addition to organic UV filter substances, comprise (a) antioxidants and/or agents which trap radicals or other photochemical reaction products and/or (b) inorganic pigments of the kind mentioned above, i.e. UV absorbers, UV reflectors and the like.

[0032] Sunscreen (or antisun) compositions prepared according to the invention, an example is more fully described below, permit retention of sufficient protection factors even in the event of intentional or unintentional wetting of the parts of the body to which they have been applied. This is not only advantageous in economical terms, but further limits or eliminates the risk of accidental "sunburn" for users who forget to reapply the product to the body.

[0033] Although the present invention is particularly relevant with respect to sunscreen formulations it is not limited to those formulations. The use of 1,2-pentanediol is likewise effective in connection with cosmetic or dermatological formulations comprising as cosmetic and/or dermatologically active agent(s):

- at least one antioxidant like Green Tea catechins, beta Carotene, Polyphenols, Rosemary extract, anti-oxidative Glycosides, Arbutin, Ascorbic Acid and derivatives thereof, Asiaticoside, Caffeic Acid, Ergothioneine, Ferulic Acid, Glucosylrutin, Hydroquinone, Isoquercitrin, Rosmarinic Acid, Rutin, Tocopherol and Tocopheryl Acetate; and/or
- at least one anti-inflammatory compound like Bisabolol, Oat Extract, Willowherb extract, Arnica Montana extract, Indomethacin, steroidal anti-inflammatory agents such as hydrocortisone, non-steroidal anti-inflammatory agents (NSAIDs), polyunsaturated fatty acid compounds such as the amides of 5,8,11-eicosatrienoic acid, or glycyrrhetic acid and mixtures thereof; and/or
- at least one anti-microbial compound like Farnesol, Triclosan, and mixtures thereof; and/or
- at least one antiperspirant like aluminiumchlorhydrate and/or zirconiumchlorhydrate.
- at least one fragrance compound
- at least one skin whitening compound like hydroquinone or rumex extract.

[0034] In order to further understand the present invention, the following non-limiting example concerned with sunscreen formulations is provided. All percentages are by weight unless the contrary is stated.

Example: Preparation and comparative testing of Sunscreen formulations

[0035] In table 1 is given the composition of four different sunscreen O/W formulations. Formulation 2 is a formulation according to the invention, i.e. comprises 1,2-pentanediol. Formulation 1 is a placebo or control sample. And formulations 3 and 4 comprise 1,2 propanediol and 1,2 hexanediol, respectively, i.e. 1,2 alkandiol with a lower or higher number of C atoms than pentanediol.

Table 1: Sunscreen formulations

substance:	1				2				3				4			
	Placebo	1,2-Pentanediol formulation according to the invention	1,2-Propanediol formulation	1,2-Hexanediol formulation	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage	Percentage
INCI	Percentage	Percentage	Percentage	Percentage	Supplier	Tradename	Supplier	Tradename	Supplier	Tradename	Supplier	Tradename	Supplier	Tradename	Supplier	Tradename
1.1 Oil Phase																
Sodium Dihydroxyethyl Phosphate	3.0	3.0	3.0	3.0	DRAGOCO	Dragophos S [2/918501]	DRAGOCO	Dragophos S [2/918501]	DRAGOCO	Dragophos S [2/918501]	DRAGOCO	Dragophos S [2/918501]	DRAGOCO	Dragophos S [2/918501]	DRAGOCO	Dragophos S [2/918501]
Bisabolol	0.1	0.1	0.1	0.1	DRAGOCO	Dragosantol [2/012681]	DRAGOCO	Dragosantol [2/012681]	DRAGOCO	Dragosantol [2/012681]	DRAGOCO	Dragosantol [2/012681]	DRAGOCO	Dragosantol [2/012681]	DRAGOCO	Dragosantol [2/012681]
Octyl Octanoate	5.0	5.0	5.0	5.0	DRAGOCO	Dragoxat EH	DRAGOCO	Dragoxat EH	DRAGOCO	Dragoxat EH	DRAGOCO	Dragoxat EH	DRAGOCO	Dragoxat EH	DRAGOCO	Dragoxat EH
Caprylic/Capric Triglyceride	10.0	10.0	10.0	10.0	DRAGOCO	Neutrolol [2/044115]	DRAGOCO	Neutrolol [2/044115]	DRAGOCO	Neutrolol [2/044115]	DRAGOCO	Neutrolol [2/044115]	DRAGOCO	Neutrolol [2/044115]	DRAGOCO	Neutrolol [2/044115]
3-(4 Methylbenzyliden)-Camphor ¹	4.0	4.0	4.0	4.0	Merck	Eusolex 6300	Merck	Eusolex 6300	Merck	Eusolex 6300	Merck	Eusolex 6300	Merck	Eusolex 6300	Merck	Eusolex 6300
Butyl Methoxydibenzoylmethane ¹	2.0	2.0	2.0	2.0	Givaudan Roure	Parsol 1798	Givaudan Roure	Parsol 1798	Givaudan Roure	Parsol 1798	Givaudan Roure	Parsol 1798	Givaudan Roure	Parsol 1798	Givaudan Roure	Parsol 1798
Octyl-Triazone ¹	4.0	4.0	4.0	4.0	BASF	Uvinul T150	BASF	Uvinul T150	BASF	Uvinul T150	BASF	Uvinul T150	BASF	Uvinul T150	BASF	Uvinul T150
Octyl-Methoxycinnamate ¹	4.0	4.0	4.0	4.0	Merck	Eusolex 2292	Merck	Eusolex 2292	Merck	Eusolex 2292	Merck	Eusolex 2292	Merck	Eusolex 2292	Merck	Eusolex 2292
Titanium Dioxide, Alumina, Dimethicon ²	2.0	2.0	2.0	2.0	Merck	Eusolex T 2000	Merck	Eusolex T 2000	Merck	Eusolex T 2000	Merck	Eusolex T 2000	Merck	Eusolex T 2000	Merck	Eusolex T 2000
Glyceryl Stearate	1.5	1.5	1.5	1.5	DRAGOCO	Dracorn GMS [2/008484]	DRAGOCO	Dracorn GMS [2/008484]	DRAGOCO	Dracorn GMS [2/008484]	DRAGOCO	Dracorn GMS [2/008484]	DRAGOCO	Dracorn GMS [2/008484]	DRAGOCO	Dracorn GMS [2/008484]
1.2 Water Phase																
Aqua	63.3	58.3	58.3	58.3		Water		Water		Water		Water		Water		Water
Xanthan Gum	0.5	0.5	0.5	0.5	Kelco	Keltrol	Kelco	Keltrol	Kelco	Keltrol	Kelco	Keltrol	Kelco	Keltrol	Kelco	Keltrol
Pentylene Glycol (1,2-Pentanediol)	0.0	5.0	0.0	0.0	DRAGOCO	Hydrolite 5 [2/016020]	DRAGOCO	Hydrolite 5 [2/016020]	DRAGOCO	Hydrolite 5 [2/016020]	DRAGOCO	Hydrolite 5 [2/016020]	DRAGOCO	Hydrolite 5 [2/016020]	DRAGOCO	Hydrolite 5 [2/016020]
1,2-Propanediol	0.0	0.0	5.0	0.0												
1,2-Hexanediol	0.0	0.0	0.0	5.0												
Citric Acid	0.3	0.3	0.3	0.3	Merck	Citric Acid	Merck	Citric Acid	Merck	Citric Acid	Merck	Citric Acid	Merck	Citric Acid	Merck	Citric Acid
1.3 Additional Phase																
Fragrance	0.3	0.3	0.3	0.3	DRAGOCO	Fragrance	DRAGOCO	Fragrance	DRAGOCO	Fragrance	DRAGOCO	Fragrance	DRAGOCO	Fragrance	DRAGOCO	Fragrance
1.4 Total	100.0	100.0	100.0	100.0												

remarks:
¹ UV filter substance
² inorganic pigments
for sun protection factor and water resistancy cf. table 2-5, respectively

[0036] The preparation of the respective sunscreen formulations 1-4 comprised a four step process: In the first step, an oil phase was composed by mixing the ingredients given in table 1 section 1.1. Care was taken that inorganic

EP 1 078 638 A1

pigments like Titanium dioxide, Alumina and Dimethicon were dispersed completely in the oil phase. The dispersion was heated to about 80 °C.

[0037] In an independent second step, a separate water phase comprising the ingredients according to table 1 section 1.2 was prepared by mixing the indicated components in their respective quantities. The aqueous mixture was also heated to about 80 °C.

[0038] Both oil and water phase were then combined in a third step of the process. The oil phase was mixed with an Ultra-Turrax stirrer into the water phase for about 5 minutes. The resulting oil in water dispersion was then allowed to cool down to ambient temperature (approx. 18 - 25 °C) while being gently stirred.

[0039] After the temperature of the dispersion had dropped below 40 °C, a fragrance mixture (see table 1 section 1.3) was added to complete the sunscreen formulation. The pH of the dispersions was found to be in the range from 6 to 6.5.

[0040] For testing the Sun Protection Factor (SPF) of formulations 1-4 the COLIPA method was employed which is described in the following references all of which are incorporated herein by reference in their entirety: Dr. Karlheinz Schrader, Skin Care Forum (publisher: Henkel KGaA), No. 10, December 1994, 2-8; M. Rohr et al, Parfümerie und Kosmetik 5/98, pages 12-19, Hüthig GmbH, Heidelberg (Germany); COLIPA SPF Test Method, The Recommendation of the COLIPA Task Force "Sun Protection Measurements", October 1994.

[0041] Average SPF values determined for the formulations 1-4 are given in the respective tables 2-5. For all four formulations, the addition of the alkanediols tested had only a neglectable effect on the sun protection factor as such.

[0042] For testing the water resistance of a given formulation 1-4 a test method was used which is described in the following references all of which are incorporated herein by reference in their entirety: M. Rohr et al, Parfümerie und Kosmetik 5/98, pages 12-19, Hüthig GmbH, Heidelberg (Germany); Schrader, K, Schrader, A., Die Sonnenschutzfaktorbestimmung: Prüfung der Wasserresistenz, Aktuelle Dermatologie, 20, 4, 1994. For determining the water resistancy the SPF was first measured under dry conditions ("without sunscreen formulation" vs "with sun-screen formulation") and then under shower conditions ("without sunscreen formulation" vs "with applied sunscreen formulation after immersion") as described in the stated references.

[0043] Water resistancies determined for the formulations 1-4 are given in the respective tables 2-5.

[0044] As can be derived from tables 2-5 water resistancy was significantly higher for formulation 2 comprising 1,2-pentanediol than for any other tested formulation.

[0045] Astonishingly, the water resistancy of the 1,2-hexanediol-formulation was not only lower than that of the 1,2-pentanediol but even lower than the water resistancy of the "placebo"-formulation. Formulation 3 comprising 1,2-propanediol showed a water resistancy similar to those of the placebo.

[0046] Thus, in the homologous series 1,2-propanediol, 1,2-pentanediol and 1,2-hexanediol only the 1,2-pentanediol has an water resistance imparting or improving effect.

Table 2

Sun protection factor and water resistancy: sunscreen formulation comprising Placebo according to table 1 col. "1"										
character of volunteers										
volunteer	age	sex	skin type	ITA	MED ¹	MED ¹	SPF ²	MED ¹	SPF ²	water resist- ancy %
					without sun- screen for- mulation	with sun- screen for- mulation		after immersion		
					[U/s]	[U/s]		[U/s]		
1	53	f	II	55	25	650	25.0	422	16.2	63.5
2	32	f	I	61	29	650	22.4	336	11.6	49.4
3	35	m	II	43	26	650	25.0	272	10.5	39.4
4	32	m	I	59	15	300	20.0	190	12.7	61.4
5	42	f	II	43	22	550	25.0	396	18.0	70.8
6	35	f	III	38	25	625	25.0	360	14.4	55.8
average SPF ²							24		14	
water resistancy [%]										56.7

remarks:
MED¹: minimal erythema dose
SPF²: sun protection factor

Table 3

Sun protection factor and water resistancy: sunscreen formulation comprising 1,2-pentanediol (acc. to the invention) according to table 1 col. "2"										
character of volunteers										
volunteer	age	sex	skin type	ITA	MED ¹	MED ¹	SPF ²	MED ¹	SPF ²	water resist- ancy %
					without sun- screen for- mulation	with sun- screen for- mulation		after immer- sion		
					[U/s]	[U/s]		[U/s]		
1	19	m	II	54	20	500	25.0	400	20.0	79.2
2	20	m	II	49	16	325	20.3	208	13.0	62.1
3	20	m	I	62	29	725	25.0	583	20.1	79.6
4	52	f	III	41	23	475	20.7	304	13.2	62.2
5	53	f	I	63	13	325	25.0	205	15.8	61.5
6	35	m	III	32	22	450	20.5	350	15.9	76.6
average SPF ²							23		16	
water resistancy [%]										70.2

remarks:
MED¹: minimal erythemat dose
SPF²: sun protection factor

Table 4

Sun protection factor and water resistancy: sunscreen formulation comprising 1,2-propanediol according to table 1 col. "3"										
character of volunteers										
volunteer	age	sex	skin type	ITA	MED ¹	MED ¹	SPF ²	MED ¹	SPF ²	water resist- ancy [%]
					without sun- screen for- mulation	with sun- screen for- mulation		after immersion		
					[U/s]	[U/s]		[U/s]		
1	25	m	II	45	30	600	20.0	390	13.0	63.2
2	24	m	II	48	37	740	20.0	373	10.1	47.8
3	58	f	II	47	27	660	24.4	429	15.9	63.5
4	38	f	I	64	37	740	20.0	481	13.0	63.2
5	42	m	III	41	20	480	24.0	312	15.6	63.5
average SPF ²							22		14	
water resistancy [%]										60.2

remarks:
MED¹: minimal erythema dose
SPF²: sun protection factor

Table 5

Sun protection factor and water resistancy: sunscreen formulation comprising 1,2-hexanediol according to table 1 col. "4"										
character of volunteers										
volunteer	age	sex	skin type	ITA	MED ¹	MED ¹	SPF ²	MED ¹	SPF ²	water resist- ancy [%]
					without sun- screen for- mulation	with sun- screen for- mulation		after immersion		
					[U/s]	[U/s]		[U/s]		
1	50	f	I	61	35	380	25.3	156	10.4	38.6
2	35	m	II	33	35	700	20.0	209	6.0	26.2
3	42	f	II	39	26	420	16.2	273	10.5	62.7
4	37	m	III	32	36	580	16.1	299	8.3	48.3
5	20	m	III	29	34	680	20.0	286	8.4	39.0
6	49	f	I	57	27	660	24.4	249	9.2	35.1
average SPF ²							20		9	
water resistancy [%]										41.7

remarks:

MED¹: minimal erythral dose

SPF²: sun protection factor

Claims

- Method for imparting water resistance to or improving water resistance of a cosmetic or dermatological formulation comprising at least one cosmetic and/or dermatological active agent in a cosmetically and/or pharmaceutically acceptable carrier for topical application to the skin of humans or animals comprising:
 - adding a water resistance improving effective amount of 1,2-pentanediol to said formulation.
- Method according to claim 1, wherein the cosmetic or dermatological formulation comprises at least one organic UV filter substance, the water resistance of which is improved by the presence of 1,2-pentanediol.
- Method according to claim 2, wherein the organic UV filter substance is selected from the group comprising derivatives of 3-benzylidenecamphor, of 4-aminobenzoic acid, of cinnamic acid, of salicylic acid, of benzophenone and of 2-phenylbenzimidazole.
- Method according to any of claims 1-3, wherein the cosmetic or dermatological formulation comprises coated or uncoated inorganic pigments, the water resistance of which is improved by the presence of 1,2-pentanediol.
- Method according to claim 4, wherein the inorganic pigments comprise pigments of a metal oxide.
- Method according to claim 5, wherein the metal oxide pigments are selected from the group comprising metal oxide pigments of titanium, zinc, iron, zirconium, silicon, manganese, aluminium, cerium, and mixtures thereof.
- Method according to any of claims 1-6, wherein the cosmetic or dermatological formulation comprises at least one antioxidant the water resistance of which is improved by the presence of 1,2-pentanediol.

8. Method according to claim 7, wherein the antioxidant is selected from the group comprising Green Tea catechins, beta Carotene, Polyphenols, Rosemary extract, anti-oxidative Glycosides, Arbutin, Ascorbic Acid and derivatives thereof, Asiaticoside, Caffeic Acid, Ergothioneine, Ferulic Acid, Glucosylrutin, Hydroquinone, Isoquercitrin, Rosmarinic Acid, Rutin, Tocopherol and Tocopheryl Acetate, and mixtures thereof.
9. Method according to any of claims 1-8, wherein the cosmetic or dermatological formulation comprises at least one anti-inflammatory compound the water resistance of which is improved by the presence of 1,2-pentanediol.
10. Method according to claim 9, wherein the anti-inflammatory compound is selected from the group comprising Bisabolol, Oat Extract, Willowherb extract, Arnica Montana extract, Indomethacin, steroidal anti-inflammatory agents such as hydrocortisone, non-steroidal anti-inflammatory agents (NSAIDs), polyunsaturated fatty acid compounds such as the amides of 5,8,11-eicosatrienoic acid, or glycyrrhetinic acid and mixtures thereof.
11. Method according to any of claims 1-10, wherein the cosmetic or dermatological formulation comprises at least one anti-microbial compound the water resistance of which is improved by the presence of 1,2-pentanediol.
12. Method according to claim 11, wherein the anti-microbial compound is selected from the group comprising Farnesol and Triclosan, and mixtures thereof.
13. Method according to any of claims 1-12, wherein the cosmetic or dermatological formulation comprises at least one antiperspirant the water resistance of which is improved by the presence of 1,2-pentanediol.
14. Method according to claim 13, wherein the antiperspirant is selected from the group comprising aluminiumchlorhydrate, zirconiumchlorhydrate.
15. Method according to any of claims 1-14, wherein the cosmetic or dermatological formulation comprises at least one fragrance compound.
16. Method according to any of claims 1-15, wherein the cosmetic or dermatological formulation comprises at least one skin whitening compound.
17. Method according to claim 16, wherein the skin whitening compound is selected from the group comprising hydroquinone and rumex extract.
18. Method according to any of claims 1-17, wherein 1,2-pentanediol is added in an amount of more than 0.5 percent by weight, based on the weight of the resulting formulation.
19. Method according to claim 18, wherein 1,2-pentanediol is added in an amount of more than 3 percent by weight, based on the weight of the resulting formulation.
20. Method according to claim 19, wherein 1,2-pentanediol is added in an amount in the range from 3 to 6 percent by weight, based on the weight of the resulting formulation.
21. Method for providing enhanced protection to the skin of humans or animals from the effects of ultraviolet radiation, said method comprising topically applying to the skin of the human or animal an effective amount of a sunscreen composition comprising a water resistance improving effective amount of 1,2-pentanediol.
22. Use of 1,2-pentanediol as water resistance improving or imparting agent in cosmetic or dermatological formulations.
23. Method for increasing water resistance and skin residency time of a cosmetic or dermatological formulation comprising at least one cosmetic and/or dermatological active agent in a cosmetically and/or pharmaceutically acceptable carrier for topical application to the skin of humans or animals comprising: adding to said cosmetic or dermatological formulation a water resistance improving effective amount of 1,2-pentanediol.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 6508

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 935 960 A (L'OREAL) 18 August 1999 (1999-08-18) * claims 1-28 *	1-23	A61K47/10 A61K7/42 A61K7/48
A	DE 43 20 744 A (DRAGOCO GERBERDING & CO GMBH) 5 January 1995 (1995-01-05) * the whole document *	1-23	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A61K
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 7 November 2000	Examiner Siatou, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 11 6508

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-11-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 935960	A	18-08-1999	BR 9902173 A	06-06-2000
			CN 1235014 A	17-11-1999
			JP 11269062 A	05-10-1999
			PL 331229 A	16-08-1999

DE 4320744	A	05-01-1995	WO 9501151 A	12-01-1995
			DE 59407737 D	11-03-1999
			EP 0655904 A	07-06-1995
